OXIDATION PATHWAYS FOR ASPHALT

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INTRODUCTION

Oxidation of asphalt is a major cause of pavement failure owing to hardening of the asphalt binder with accompanying changes in viscosity, separation of components, embrittlement and loss of cohesion and adhesion of the asphalt in the mix. Slow oxidation of asphalt continues during the service life of the roadbed at a rate that appears to be partly determined by the void volume of the roadbed, as well as the properties of the asphalt (1-3).

We have focused on understanding the chemical pathways for slow oxidation of asphalt in order to predict how rapidly an asphalt will oxidize, based on its composition, and to find better ways to inhibit the process under service conditions.

OXIDATION PROCESSES IN ASPHALT

Three different mechanisms proposed for asphalt oxidation include free radical oxidation, photooxidation and molecular oxidation. The first two processes may involve participation of free radicals while the last does not. The distinction is important in indicating whether phenolic inhibitors will be effective in slowing oxidation. Free radical processes are inhibited by antioxidants, whereas molecular oxidation requires removal of oxygen or the oxygen-reactive component. In very viscous bulk asphalt, added antioxidants may have limited value.

Oxidative aging is characterized by oxygen uptake, formation of sulfoxide and carbonyl bands in the IR spectrum and marked increases in dynamic viscosity and other rheological properties (4). No chemical changes are observed on heating asphalt at 60-130°C in the absence of oxygen, although small amounts of volatiles may be lost at elevated temperature, causing viscosity increases. Above 150°C non-oxidative reactions may begin to cause chemical changes, even without oxygen.

Nmr-derived average structures for SHRP core asphalts (4), two of which are shown in Figure 1, illustrate the point that oxidative aging in asphalts is not a single chemical process, but a composite of several independent and concurrent oxidation reactions at several sites in the asphalt structure. These reactions affect families of similar structural units. Therefore, to understand the process at the molecular level, we must rely for guidance on the behavior of model compounds and model probes. Moreover, the interactions of oxidation products with polar groups in asphalt lead to large changes in physical properties and can strongly affect service life.

Studies of the thermal oxidation of asphalt over the past thirty years have almost uniformly concluded that asphalts are not protected from oxidation by addition of most autooxidation inhibitors such as hindered phenols or zinc dithiocarbamates (5, 6) and that free radicals play no role in the oxidation process. This conclusion is based on a concept of free radical oxidation as it applies to reactive hydrocarbons where oxidation proceeds by way of long

chains. In asphalt, native phenol inhibitors already are present and asphalt oxidation may still involve free radicals, but not a chain oxidation.

SULFUR CHARACTERIZATION AND OXIDATION

Sulfur oxidation to sulfoxide is easily measured in asphalt by a single band in the IR near 1000 cm^{-1}. Many investigators have used sulfoxide formation as a measure of asphalt aging, but without clear evidence for the role of sulfoxides in the aging process or the relation of this oxidation to other oxidative changes in the asphalt such as carbonyl formation.

SHRP core asphalts have total sulfur contents ranging from 1 to 8 percent. Thermal oxidation at 50°-100°C converts a fraction of the total sulfur to sulfoxide (>SO) corresponding to conversion of aliphatic sulfide (>S) to >SO. Figure 2 shows that the concentration of >SO formed in asphalts heated in the TFOT correlates well ($r^2 = 0.95$) with the original concentration of S, but accounts for only 20-30 mole percent of it. The >SO formed by chemical oxidation accounts for a higher proportion of S in high S asphalts.
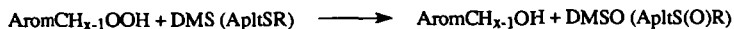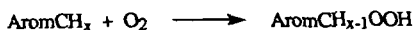
Sulfur K-edge X-ray Absorption Fine Structure (XAFS) spectra were used to characterize sulfur in several different unoxidized and oxidized asphalts (S). Analysis of the XAFS data are summarized in Table (1). Unoxidized samples of asphalts show the presence of only two kinds of sulfur: aliphatic sulfide and thiophenic sulfur in the ratio of 22:78 to 40:60; among unoxidized asphalts, only AAG-1 and AAM-1 show the presence of any sulfoxide. Comparison of XAFS and ESCA spectra for AAA-1 shows good agreement on the ratios of sulfide and thiophenic sulfur.

Thermally oxidized AAA-1, AAG-1 and AAK-1 show formation of sulfoxide which is derived only from sulfide sulfur. About 32 and 14% of AAA and AAK sulfides respectively disappear on oxidation, part of which is accounted for by sulfoxide, however in AAG, 51% of sulfide oxidizes to give the expected amount of additional sulfoxide. No other oxidized sulfur species was observed.

In a sample of AAG oxidized with t-BuOOH no sulfide sulfur remains after oxidation, consistent with the low initial concentration of sulfide sulfur in AAG- of 0.13 M and with the finding that thermal oxidation of AAG-1 gives only 0.15 M sulfoxide. Asphalt AAA-1 has 10 percent sulfide left after chemical oxidation with the difference almost all accounted for by sulfoxide. AAM-1 is especially interesting in having the lowest proportion of sulfide of any sample examined by XAFS; thermal oxidation AAM also gives the smallest amount of sulfoxide by IR.

Model compounds dimethylsulfide, di- n-butyl sulfide and dibenzyl sulfide (DMS, NBS, DBS) were used to study thermal oxidation of aliphatic sulfide sulfur in asphalts. Neither DMS, NBS nor DBS oxidized alone with oxygen at 100°C. By implication, >SO formation in asphalts must occur indirectly. DMS and NBS were added to AAA or AAG to probe the pathway for sulfoxide formation from aliphatic sulfides under conditions where direct oxidation is not detectable. A mixture of DMS and AAA-1 heated for three days at 110°C in air in a sealed tube developed a strong IR band near 1000 cm^{-1} due to DMSO. Similar experiments with 0.05-0.1 M NBS in asphalt gave similar results when analyzed by IR and by GC for Bu$_2$SO. Preoxidized AAG also oxidized NBS. The results clearly demonstrates that a peroxy intermediate (probably non sulfur) species which forms with oxygen can be intercepted by DMS or NBS.

One candidate for this oxidation species is peroxide or a hydroperoxide formed from reactive pyrrolic NH bonds or benzyl CH bonds.

$$\text{AromCH}_x + O_2 \longrightarrow \text{AromCH}_{x-1}\text{OOH}$$

$$\text{AromCH}_{x-1}\text{OOH} + \text{DMS (ApltSR)} \longrightarrow \text{AromCH}_{x-1}\text{OH} + \text{DMSO (ApltS(O)R)}$$

However, purified cumene (isopropylbenzene, CuH) was heated in oxygen at 110°C for three days with DMS gave no DMSO. This experiment shows that whatever the reactive oxidation centers might be, they are much more reactive to oxygen than cumene CH bonds.

The effect of oxygen pressure on rates of oxidation of sulfide was examined in AAA-1 thin films by heating samples in air or oxygen at 100°C and comparing the FTIR band for sulfoxide between 1100 and 960 cm^{-1}. The oxygen reaction was clearly faster by a factor of at least two and perhaps more, depending on the extent of conversion of alkyl sulfides in AAA-1. Although these data are consistent with rate-limiting oxygen diffusion, we find no significant difference between oxidation rates in thin films and lumps.

We have also measured the stability of several asphalt sulfoxides by first oxidizing asphalts at 100°C for 20-30 hrs and then heating them under argon in sealed tubes for 5-10 hrs at 165°C followed by FTIR analyses. Argon heated samples showed about 10-58 percent less >SO than unheated ones, indicating a modest degree of stability for >SO under TFOT conditions. The fastest >SO loss rate corresponds to a half life of 6 hrs at 165°, consistent with half lives found by Walling and Bullyky (6) for pyrolysis of long chain aliphatic sulfoxides. Table 2 summarizes >SO decomposition data.

OXYGEN UPTAKE AND BALANCES IN OXIDIZED ASPHALT

Oxygen and Product Balances

We have conducted detailed oxygen uptake and product studies on the four inner core asphalts AAD-1, AAG-1, AAK-1 and AAM-1 to evaluate how well the observable products including >SO and >CO account for the absorbed oxygen. In each case we examined the oxidation of both the tank asphalt and the TFOT asphalt which had been heated in air for 5 hours at 165°C (WRI supplied these samples). We oxidized several samples of these asphalts as thin films at 100°C in air for times as long as 409 hrs. We measured oxygen uptake for each sample and quantitatively measured >SO and >CO formation by FTIR to find out how much absorbed oxygen is accounted for by these two classes of products.

Table 3 summarizes the average oxidation product and rate data. The most important qualitative conclusions are that oxygen balances are generally low (20-60%), that carbonyl forms in low yield in most asphalts, but not in AAM or AAMT where sulfide is very low, and that there are no significant differences between tank and TFOT samples, again except for AAM and AAMT. The ratio of >SO/>CO is close to 10 in oxidized K and KT samples, whereas this ratio is closer to 3 or 4 in D and DT. Both asphalts have relatively high total sulfur, but D(DT) has a higher proportion of sulfide sulfur than does K (46% vs 36%). The 409 hr AADT experiment was analyzed for CO and CO_2 formation as well as oxygen uptake, but none could be found under conditions where we estimate we could detect <3 μmoles. Thus the missing oxygen is still largely in the asphalt, perhaps as water.

Uncertainty in oxygen uptake and product measurements is ±20% in O_2, ± 10% in >SO formation and possibly as high as ± 100% in >CO. The high uncertainty in >CO stems mainly from our uncertainty as to which model ketone standard to use for calibration of the FTIR spectrum around 1700 cm^{-1}. We chose valerophenone as a standard assuming that any ketones would form at benzylic positions and these would be well modeled by valerophenone. However, oxidation of phenols also leads to ketone formation (as cyclohexadienones) which

probably have very different IR spectral cross sections from arylphenones such as butyrophenone. But, even doubling the carbonyl concentrations still leaves oxygen balances short of the 2:1 stoichiometry for each O_2 to form one >SO or >CO and one ROH or H_2O.

Oxidation and Product Rates

Table 3 also shows average rates of oxygen uptake, normalized for time and sample size in micromoles mg^{-1} hr^{-1}. The striking feature of these data is the similarity in rates for all of the asphalt samples, with few exceptions. The rates are close to 5 x 10^{-3} micromoles mg^{-1} hr^{-1} for oxygen uptake; hardly a two-fold difference in rates among all asphalts studied even though AADT and AAKT have 1.2 M and 0.76 M sulfide sulfur compared with AAGT and AAMT with only 0.14 M and 0.065 M sulfide. Again diffusion limited oxidation is one explanation.

DISCUSSION

Sulfur oxidation is widely investigated in asphalts because the IR fingerprint for sulfoxide is so easy to measure, but the details of the process and the kinetics have been confused by several conflicting ideas about the origins of the reaction. The data from this study using XAFS and ESCA spectroscopies clearly shows that only aliphatic sulfide sulfur is oxidized during thermal oxidation or mild chemical oxidation by t-BuOOH; thiophenic sulfur is not significantly affected during these oxidations. This conclusion, first reached by Ruiz et al (7) and by Petersen et al. (8) for a few kinds of asphalts has now been extended semi-quantitatively to the SHRP core asphalts and by implication to all other asphalts as well.

It now becomes clearer why >SO-time curves for oxidation of different asphalts are so different and why asphalts with similar total sulfur content, but with different aliphatic:aromatic distributions of sulfur give different >SO yields. In the case of low sulfur asphalts, such as AAG or AAM, aliphatic sulfide is rapidly exhausted and formation of >SO almost stops after 30 hrs at 100°C. High aliphatic sulfide sulfur asphalts such as AAA or AAD continue to form much higher proportions of >SO for longer times.

The induced oxidation of DMS and NBS in oxidizing asphalt points to formation of an peroxy intermediate from direct interaction of asphalt with oxygen. Induced oxidation of NBS is found in both AAA and AAG asphalts, indicating that the source of the peroxy intermediate is both independent of the sulfur and in excess of sulfide sulfur, at least in AAA. Oxygen effects on rates of formation of >SO also are in qualitative agreement with this hypothesis.

Rates and products in oxidation of core asphalts points to oxygen imbalances in terms of the >SO and >CO products; in some cases the deficits are large. Rates of oxidation show a striking similarity among the four core asphalts even though they differ by twenty-fold in sulfide content and almost as much in vanadium and other metal ion contents. Oxidation rates do not appear to be controlled by these components, but by other components such as phenols or dihydroaromatic groups, the identity of which are currently under investigation. Other features of the rate and product studies also fit well with the overall concept. Thus we see that AAM or AAMT oxidize rapidly to form >SO but the oxidation continues after >SO production stops due to exhaustion of the aliphatic sulfide to form much more carbonyl. In that sense sulfide sulfur acts as internal redox inhibitor to limit >CO formation from the peroxy intermediate.

Figure 3 shows a schematic representation of the oxidation process. In this scheme, the first step forms peroxy intermediate which then can oxidize either sulfur and form >SO and an alcohol, or in the absence of sulfide sulfur, the intermediate may form carbonyl by one of several paths. Alcohols are difficult to detect and might account for part of the missing oxygen.

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Table 1. Analysis of Sulfur XAFS and ESCA Spectra of Asphalt Samples[a,b]

Sample	%Sulfide (M)	(%ΔS)[c]	%Thiophene	%>SO Sulfoxide	(%Δ>SO)[d]	% S(M)
AAA-1	40[34][e]	–	60(66)[e]	–	–	7.3(2.3)
AAA-1 oxid[f]	27[24][e]	13	67	6	-7	7.3
AAB-1	31	–	69	–	–	5.6(1.75)
AAC-1	25	–	75	–	–	2.7(0.84)
AAD-1	46(1.2)	–	54	–	–	8.6(2.7)
AAF-1	28	–	72	–	–	3.5(1.1)
AAG-1	33(0.14)	–	59	8	–	1.3(0.41)
AAG-1 oxid[f]	15	18	60	25	-1[h]	1.3
AAK-1	36(0.76)	–	64	–	–	6.6(2.1)
AAK-1 oxid[f]	31	5	62	7	+2	6.6
AAM-1	17(0.065)	–	78	5	–	1.2(0.38)
Asph-X(AAA-1 oxid)[g]	10	30	63	27	-3	7.3
Asph-Y(AAG-1 oxid)[g]	0	33	53	17	+23	1.3

[a]Data from G. P. Huffman et al. (7). [b]Samples from WRI except X and Y from SRI. [c]Change in sulfide. [d]Difference between ΔS and >SO. [e]ESCA spectra taken at SRI. [f]Oxidized by heating at 113°C for 120 h. [g]Oxidized with t-BuOOH in cyclohexane at 25°C.

Table 2. THERMAL CHANGES IN SULFOXIDE AND CARBONYL IN PREOXIDIZED ASPHALTS IN ARGON AT 165°

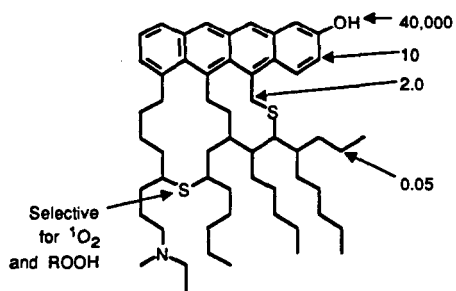| Asphalts (≥SO, M)	Time, hr	% Change >SO	% Change >CO
NBSO[a] (0.29 M)	5	-58	–
AAD	7	-38	–
AAGT (0.19 M)	5	-7	+44
AAGT (0.19 M)	10	-7	+60
AAK (0.37 M)	5	-48	+12
AAK (0.37 M)	10	-54	+7

[a]Dissolved in unoxidized AAD.

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Table 3. OXYGEN UPTAKE AND BALANCES FOR ASPHALTS[a]

Sample	Timee (hr)	Wt Sample (mg)	Products, umoles				
			$\Delta\Delta O_2$	>SO	>CO	%OB[b]	10^3 Oxld Rate, μmols/mg hr
D	114	79	38	13	4.1	23	4.2
DT	409	100	105	37	7	22	2.5
G	30	113	14	13	–	–	4.2
GT	140	184	61	34	12	38	2.3
K	24	86	7	13	1.0	100	3.4
KT	140	392	79	141	32	108	1.5
M	120	261	205	80	114	47	6.5
MT	120	250	74	76	121	130	2.5

[a]Oxidized in air as thin films at 100°C.
[b]OB = oxygen balance = [(>SO + >CO)/2ΔO_2] x 100.

OH ← 40,000
— 10
← 2.0

Selective
for $^1O_2$
and ROOH

0.05

AAK-1 (6% S)

OH ←
10
40,000
1.0
0.05
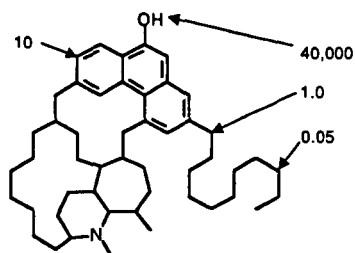
AAG-1 (1% S)

* From P.W. Jennings, Montana State University.

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Figure 1. Oxidizable structures in representative asphalt molecules with
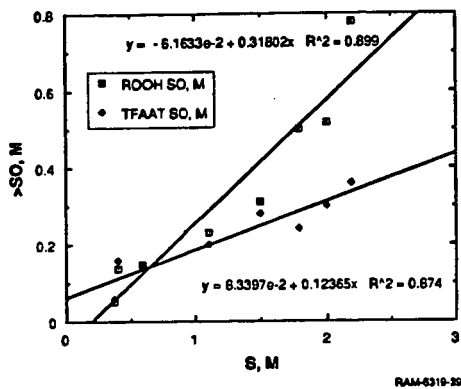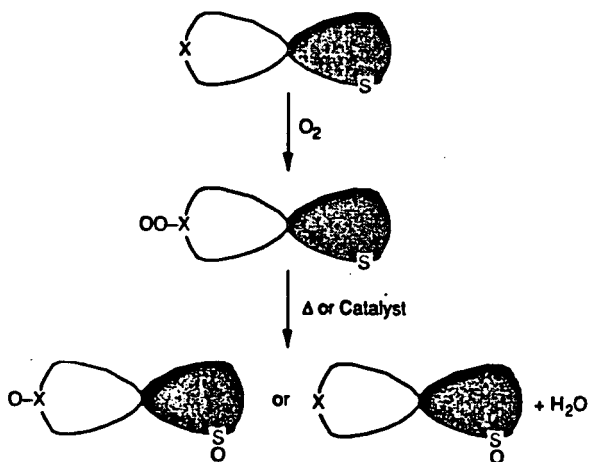relative reactivities shown for $RO_2\cdot$ radicals (11).

Figure 2. Correlation of >SO with S in core asphalts.

Figure 3. Possible pathways for >SO formation.

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